New Highly Efficient Method of Polyoxometalate (POM) Catalyzed Ozone Bleaching of Industrial Eucalypt (*E. globulus*) Kraft Pulp

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Abstract. The highly efficient and selective environmentally benign bleaching approach using polyoxometalate (POMs) catalyzed ozonation of chemical pulps in organic solvent reaction media has been developed. The Keggin-type molybdovanadophosphate heteropolyanions (HPAs) showed a well-defined capacity for ozonation improvement in the presence of number polar low-boiling aprotic and protic organic solvents. Under optimized conditions, the solvent-based HPA-catalyzed ozone bleaching of industrial eucalypt kraft pulp showed remarkable brightness improvement by 15.1% ISO, with additional lignin removal by 39.4% and increase in intrinsic viscosity by 3% in comparison with conventional ozone bleaching technique.

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Introduction

The environmental concern related to pollutant commercial chlorine-based pulp bleaching technologies along with the increased market demand for totally chlorine-free (TCF) and low AOX (absorbable organic halogens) pulps caused substantial interest to non-chlorine oxidative bleaching chemicals such as oxygen, hydrogen peroxide and ozone. Ozone is the most powerful and particularly potential oxidation agent for chemical pulp bleaching [1]. However, the low selectivity of ozone treatment towards lignin (due to unwanted reactions with carbohydrates) restricts delignification capacity of ozone and limits substantially its further commercialization [2].

The selectivity improving of ozone bleaching can be solved by use of efficient catalytic systems such as polyoxometalates (POMs), which have a wide application as versatile green catalysts for liquid-phase oxidation of different organic substances [3]. Heteropolyoxometalates (free acids and salts of heteropolyanions) possessing the properties of both strong acids and very efficient oxidants hold a great interest now for application like bi-functional catalysts in homogeneous and heterogeneous systems [4,5]. The high HPAs solubility in water and oxygen containing organic solvents, the high HPAs stability over a wide temperature and pH range and, finally, the HPAs ability of easy regeneration by various oxidants have made possible their use as efficient catalysts for selective delignification of wood and pulp [6-8]. The α-Keggin type mixed-addenda HPAs, such as molybdovanadophosphate heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$, were recognized as the more suitable POMs for oxidative (dioxygen) delignification.

In the present communication, the results on development of a novel bleaching approach using POM-catalyzed pulp ozonation in organic solvents as the additives to reaction solution are reported.

Experimental

Commercial unbleached eucalypt (*E. globulus*) kraft pulp with 41.6% ISO brightness, 2.4% residual lignin (as Klason and acid-soluble) and 1320 mL/g intrinsic viscosity was used. Molybdovanadophosphate heteropolyanion HPA-5 was synthesized according to a previously described procedure [9]. Pulp ozonation (low consist.) was performed using Fischer laboratory ozonation system equipped with a Fischer-502 ozone generator, 2L glass batch reactor and high-speed Teflon-covered stirrer.
Residual lignin content (as Klason and acid-soluble) was determined according to TAPPI T 222 om-88 and UM 250. Pulp viscosity was measured in CED according to SCAN-CM 15:88. Pulp physical properties were examined according to TAPPI T 220 om-88. ISO brightness and DIN 6167 C/2 yellowness index were measured by CM-3630 Spectrophotometer (Minolta). The aldehyde groups in pulps was measured spectroscopically (Shimadzu, UV-160A) after color reaction with 2,3,5-triphenyltetrazolium chloride. Hexenuronic acid (HexA) groups were quantified by selective hydrolysis in formic acid-sodium formate buffer followed by UV-spectroscopy of the formed 2-furoic acid.

Results and discussion

A series of low-boiling polar aprotic (acetone and dioxan) and protic (methanol, ethanol, *n*-propanol and isopropanol) organic solvents were chosen as a potential reaction media for POM-catalyzed ozone bleaching of chemical pulps. For solvent screening experiments, the industrial eucalypt (*E. globulus*) kraft pulp was ozonated under fixed conditions of ozone charge and catalyst (HPA-5) concentration in the presence of 6% (w/w) of organic solvent. The brightness development as well as the extent of lignin and carbohydrate degradation during ozonation was examined and compared with control (solvent-free) test.

Table 1 - Results of POM catalyzed ozonation of eucalypt (*E. globulus*) kraft pulp in various reaction media

Reaction medium composition	Brightness (%ISO)	Residual lignin (% odp)	Intrinsic viscosity (ml/g)	Tear Index (mN m^2/g)	Burst Index (kPa m^2/g)	Tensile Index (N m/g)
Water (catalyst-free)	53.18	1.83	920	3.86	0.12	3.02
POM/water	53.42	1.75	951	4.14	0.15	3.51
POM/water/methanol	55.76	1.54	970	4.43	0.16	3.98
POM/water/ethanol	55.22	1.58	1035	4.43	0.15	4.21
POM/water/acetone	56.84	1.42	950	4.16	0.18	4.58
POM/water/dioxane	55.78	1.59	1026	4.52	0.21	4.44
POM/water/1-propanol	54.08	1.81	1028	4.27	0.19	4.08
POM/water/isopropanol	51.72	1.78	1017	4.08	0.17	4.31

As can be seen from Table 1, the conventional pulp ozonation in water medium (control test) caused substantial drop in pulp viscosity (by 30.3%) with respective loss in strength properties, indicating intensive carbohydrate degradation. Similar to previously reported observations, the presence of POM (HPA-5) in aqueous solution has positive effect on selectivity of pulp ozonation, somewhat decreasing residual lignin content and increasing pulp viscosity. But the pulp brightness, as the most important bleaching property, is only slightly affected.

It is evident that the addition of organic solvent into the reaction mixture substantially improves POM-promoted ozonation. Even moderate solvent proportion of 6% (w/w) in aqueous solution caused additional gain in brightness up to 3.4% ISO with simultaneous increase in pulp viscosity up to 8.8% and lignin removal up to 18.9% in comparison with POM/water and, particularly, with control (water, catalyst-free) ozonation. Obviously, the bleaching effect depends on kind of organic solvent used. Four tested solvent-based reaction systems, i.e., methanol-, ethanol-, acetone- and dioxane-based, showed significant advantage over the conventional (water) as well as POM/water ozonation. The *n*-propanol and isopropanol showed the lowest bleaching impact, while the methanol and, particularly, acetone solution was found to be the best reaction media in terms of pulp brightening and delignification.

The POM/ethanol solution showed the highest ozonation selectivity (Figure 1), as a measure of polysaccharide degradation and expressed as lignin decrease per unit of viscosity decrease, followed by dioxane, acetone and methanol solutions.

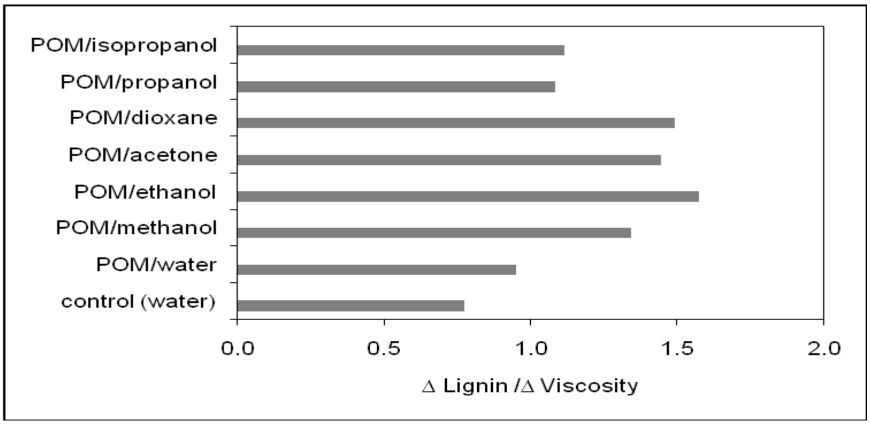

Figure 1 - Selectivity of POM-catalyzed pulp ozonation in organic solvent reaction media.

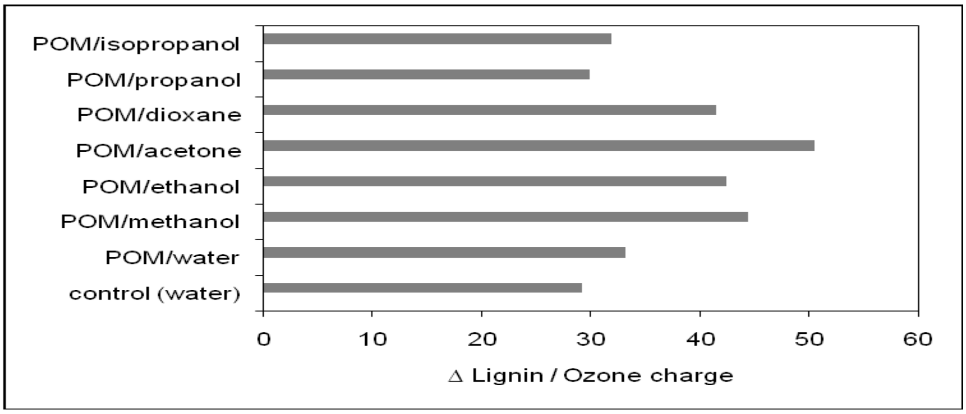

Figure 2 - Delignification efficiency of POM-catalyzed pulp ozonation in organic solvent reaction media

The highest ozonation effectiveness in terms of pulp delignification or lignin removal (Figure 2) was shown in POM/acetone medium (50.5% over 33.1% for POM/water), followed by methanol (44.45%), ethanol (42.5%) and dioxane solutions (41.5%).

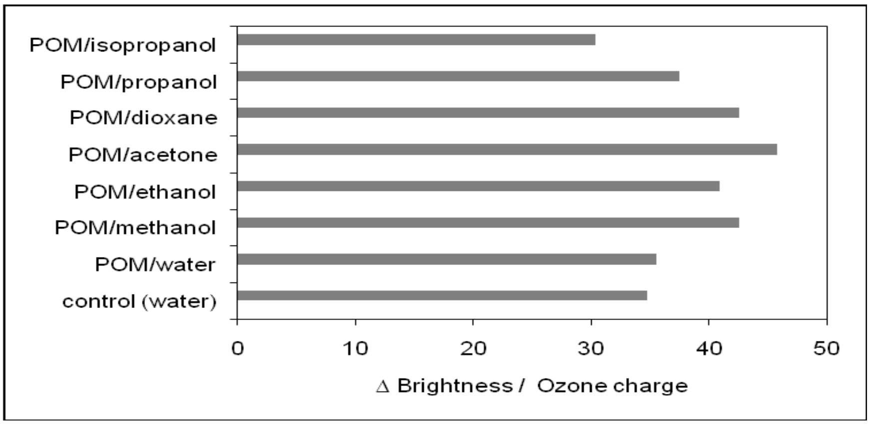

Figure 3 - Brightening efficiency of HPA-catalyzed pulp ozonation in organic solvent reaction media

Finally, the ozonation effectiveness in terms of pulp brightening or brightness improvement (Figure 3), commonly used as a measure of relative pulp bleachability and expressed as increase in brightness per unit of applied active bleaching chemical, was also the highest in POM/acetone solution (45.8%), followed by dioxane (42.6%), methanol (42.6%) and ethanol (40.9%), over 35.5% for POM/water.

The elevated intrinsic viscosity of pulps ozonated in POM/solvent media is directly related to their better strength properties (Table 1). The tearing, bursting and tensile indexes of these pulps are notably higher than those found for control (water) and POM/water ozonation and near the strength indexes of untreated (unbleached) pulp.

Based on the results of solvent screening experiments, the acetone-water reaction media was chosen for further studies of POM-catalyzed pulp ozonation. The effect of solvent content and catalyst concentration was examined.

As shown in Table 2, the increase in solvent content in the reaction mixture caused impressive increase in pulp brightness and degree of delignification. A rise in solvent proportion from 6% to 60% (w/w) led to gain in brightness by 15.1% ISO and to additional lignin removal by 39.4% in comparison with POM/water ozonation. The ozonation improvement was particularly intensive with solvent proportion above 40% (w/w).

Increase in solvent content up to 40% (w/w) had also protective effect on carbohydrates, increasing by ca. 3% pulp intrinsic viscosity and significantly improving the selectivity of ozonation in comparison with POM/water solution, as a result of scavenging by solvent of active oxygen-centered radical species formed during ozonation. The further increase in solvent proportion caused substantial drop in pulp viscosity, apparently due to increased activity of acid-catalyzed solvolytic processes [10].

The strongest catalytic effect of POM on ozonation reaction was noted under 1mM catalyst concentration in the reaction solution. The subsequent increase in POM concentration inhibited pulp delignification and brightening, decreasing thereby the efficiency of ozonation as a whole. The structural and redox changes of HPAs under acidic reaction conditions are the reason of the observed effect of marginal catalyst concentration needed for successful pulp ozonation [11].

Table 2 - Effect of organic solvent (acetone) content and catalyst (POM) concentration on ozonation of eucalypt (*E. globulus*) kraft pulp

Reaction variables	Brightness (%ISO)	Residual lignin (% odp)	Intrinsic viscosity (ml/g)	Tear Index (mN m^2/g)	Burst Index (kPa m^2/g)	Tensile Index (N m/g)
6% (w/w) acetone	56.84	1.48	950	4.16	0.19	4.58
20% (w/w) acetone	58.50	1.46	963	3.55	0.19	4.83
40% (w/w) acetone	60.82	1.34	976	3.91	0.22	5.75
60% (w/w) acetone	68.48	1.06	851	4.09	0.22	6.09
0.5 mM POM	58.50	1.46	963	3.55	0.19	4.83
1.0 mM POM	59.50	1.29	967	3.26	0.20	4.64
2.0 mM POM	57.44	1.57	1015	3.62	0.21	4.24
4.0 mM POM	55.06	1.74	1051	3.79	0.23	4.01

The change in solvent and catalyst concentration had no essential effect on the physical (mechanical) properties of ozonated pulps (Table 2). The minimal changes in bursting and tearing pulp strength are within the range of standard deviation. At the same time, it is clear that the tensile strength of ozonated pulps is better under higher solvent and lower POM concentrations.

Conclusions

The polyoxometalate (POM) catalyzed ozonation of chemical pulps in organic solvent media was found as a particularly effective and selective environmentally benign bleaching approach providing a way for substantial increase in pulp brightness, viscosity and degree of delignification of bleached pulps in comparison with other known ozonation techniques. The remarkable gain in brightness by 15.1% ISO, degree of delignification by 39.4% and viscosity by 3% (as compared with conventional ozone bleaching) was achieved under optimized conditions of POM-catalyzed ozonation of commercial eucalypt kraft pulp in acetone/water reaction media.

Acknowledgements

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